

### General Introduction

#### *Highlight*

This chapter presents a concise account on polyurethane, its preparation, characterization, property evaluation and its applications. Special emphasis is given on bio-based, biodegradable and sustainable polyurethane as an eco-friendly polymeric material. Considering the importance of polyurethane nanocomposites, a brief review has been made on different nanomaterials, fabrication techniques and potential applications of polyurethane nanocomposites in different domains of material science. A brief description on different spectroscopic and analytical techniques used in the characterization of polyurethane, different nanomaterials and their nanocomposites is further *delved into*. Lastly, the chapter includes scopes, objectives and plan of research for the present study.

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Part of this chapter is ready for communication as

**Gogoi, S., & Karak, N.** Bio-based biodegradable waterborne polyurethane nanocomposites as sustainable materials: A review.

## 1.1. Introduction

Since inception, polymer has been the subject of attraction for the researchers due to its large contribution towards mankind. Civilization started with stones, passed the metal and bronze ages and now progressing through the polymer age.<sup>1</sup> In the nineteenth and twentieth centuries, extensive research has been exercised to develop polymer as the advanced material for future. Such efforts along with the technological advances bring a huge impact in the domain of polymeric materials.<sup>2,3</sup> Nowadays, polymer finds numerous applications ranging from advanced utility in aerospace, automotive, electronics, biomedical to day-to-day common utilization in the form of adhesive, sealant, coating or packaging material. However, high rate of polymer consumption due to its vast acceptability and fast growing human population have put certain concerns over safe use of polymeric materials.<sup>4</sup> In most of the time, polymers have been designed with limited consideration to their ecological footprint, especially relating to their ultimate disposability. High level of consumption results accumulation of polymeric materials on the earth surface causing severe damage to the fragile eco-system.<sup>5</sup> On the other hand, pure petroleum based production has put stark pressure on the ever depleting crude oil feed stock.<sup>6,7</sup> Therefore, it is the high time to take responsibility in order to address these basic glitches through the expansion of novel bio-based, biodegradable, eco-friendly polymeric materials.

The concept of synthetic biodegradable polymer was first put forwarded in 1980's.<sup>8</sup> Biodegradable polymers are those which provide stable and durable service life during use, while undergo destruction after use in response to the stimuli of certain environmental triggers. Such triggers could be microbial, hydrolytically or oxidatively susceptible linkages built into the backbone of the polymer, or use of some external entities that catalyze breakdown of the polymer chains under specific environments.<sup>9</sup> Generally, synthetic polymers with hydrolysable linkages are known susceptible for biodegradation process. These include polyesters, polyglycolic acid, polycaprolactone, polyamides etc.<sup>10</sup> In this context, polyurethane (PU) is known as one of the most promising macrostructures with acceptable biodegradability. PU was first introduced years back in 1937, although its biodegradability came to light only after its commercial production.<sup>11,9</sup> From chemistry point of view, PU is a rearrangement product form in a reaction between di/poly-isocyanate and di/polyol

compounds. The most unique feature of PU is its wide range of physical and chemical properties, which can be tailored to meet the highly diversified demands of modern applications such as coatings, adhesives, fiber, foams, biomaterials etc.<sup>12</sup> PU consists of three basic components, *viz.* di/poly-isocyanate, di/polyol and chain extender. Generally, extent of biodegradation depends on the chemical nature of these components.

In addition to bio-disposability, synthesis of PU often offers the scope to utilize bio-based renewable raw materials.<sup>13,14</sup> Such processes are technically and economically practicable, which impart high eco-friendly attributes to the resultant material. Generally, plants present the largest renewable resources. Estimation has shown that around 120 billion tons carbon in biomass equivalent to more than 80 billion tons of oil equivalents (toe) are produced globally in a year.<sup>15</sup> Utilization of even small fraction of these bio-resources can dramatically reduce the stress on ever depleting petroleum feed-stock. Art of literature advocates successful use of different vegetable oils like castor oil, sunflower oil, linseed oil, nahor oil, soybean oil etc.; carbohydrates like sucrose, starch, cellulose, chitin, isosorbide etc.; polyphenolic compounds like lignin etc. for the sustainable development of PU.<sup>16-25</sup> In addition to the benefit of sustainability, use of bio-based materials creates other favorable niche as well. Most of the bio-based PUs exhibit enhanced biodegradability and profound cytocompatibility, which create avenue for their biomedical applications. On the other hand, technological advancement further makes it possible to obtain water dispersible PU (WPU) by replacing volatile organic solvents.<sup>26</sup> Such type of PU system is particularly useful to restrict release of carbon to the atmosphere during its synthesis, processing and application.

Besides chemical structure, the architectural features of a polymer also confer many unique properties.<sup>27</sup> In this milieu, hyperbranched PU (HBPU) has been discussed substantially in recent time to design advanced polymeric materials with unique properties. A hyperbranched polymer consists of three basic units, *viz.* dendritic, linear and terminal, which are arranged in a random fashion along the polymeric backbones.<sup>28</sup> The branches of hyperbranched polymer are stretched in all directions, which results in the formation of a three dimensional, divergent and highly branched globular structure. The periphery of the polymer contains a large

number of terminal functional groups. Hyperbranched polymer offers many unique features like three dimensional globular, non-entangled inimitable structure, low intrinsic viscosity, high solubility, large surface functionalities etc.<sup>29</sup> These properties are comparable to those of dendrimer, the perfectly branched macromolecular structure of dendritic polymer family.<sup>29</sup> Hyperbranched polymer also provides facile one-pot synthetic process in a large scale, which increases its importance in industry and academia.

As mentioned earlier, PU possesses versatility in terms of its properties and applications. Despite of the fact, in many occasions modification is required to accomplish the demand of modern day applications. Conventionally, window of widespread properties of PU can be broadened by physical and chemical modifications like blending, creating cross-linking reaction or forming an interpenetrating network etc.<sup>30</sup> However, nanotechnology based approaches have over taken the conventional routes in recent years. It has been found that incorporation of even minute amount of nanomaterial (>5 wt%) to a polymer matrix can boost the material properties dramatically.<sup>31</sup> Literature reveals use of different types of nanomaterials of organic and inorganic origin to prepare PU nanocomposites (PUNC). The most highlighted nanomaterials are belong to carbon family, which includes carbon nanotube (CNT), graphene based nanomaterials like graphene oxide (GO), reduced graphene oxide (rGO) and most recently carbon dot (CD).<sup>32,33</sup> On the other hand, inorganic nanomaterials include different metals and metal oxides, such as iron oxide ( $\text{Fe}_3\text{O}_4$ ), silver (Ag), titanium oxide ( $\text{TiO}_2$ ), nickel ferrite ( $\text{NiFe}_2\text{O}_4$ ); inorganic minerals such as hydroxyapatite (HAp); different nano clays etc.<sup>34</sup> Fabrication of PU with these nanomaterials often lifts up the inferior properties without hampering the superior ones. These PUNC have been used in different domains, e.g. coating, biomedical, electrical, opto-electronic, catalytic etc.<sup>35-38</sup> In many occasions, multiphase nanohybrid systems (e.g. organic/inorganic nanohybrids) are used to gather the benefits of different nanomaterials within a single system.<sup>39</sup>

Thus, the initial assessment reveals the importance of designing of high performing, eco-friendly PUNCs in the scenario of current environmental concerns and modern day demands for advanced material. In this milieu, development of bio-based, biodegradable, low volatile organic compound (VOC) containing HBPU

nanocomposites may provide a proper research proposition to tackle economic, environmental and ecological issues related to conventional polymeric materials.

## 1.2. Background

PU was first introduced in 1937 by Otto Bayer in IG Farben laboratory, Germany.<sup>11</sup> Initially this polymer was used in military and aerospace applications. The commercial production of PU had started in 1940, though its expansion as a utility material started after 1950 with the improvement of its elastic properties.<sup>40</sup> In 1952, poly-isocyanates were commercially available in the market and in 1954, production of flexible PU foam started by using toluene diisocyanate and polyester polyol as the structural components.<sup>40</sup> At the same time, Dupont introduced a Spandex fiber called Lycra, which was a PU based on poly(tetramethylene glycol), 4,4-diphenylmethane diisocyanate and ethylene diamine.<sup>40</sup> With the introduction of low cost polyether polyol, a major change in PU research was achieved. In the 1990s, the US Navy started the use of new two-component PU and hybrid poly(urethane urea) elastomers, which were applied for spray-in-place load bed liners and military marine applications.<sup>40</sup> During the past years, PU has passed through a chronological development with introduction of new raw materials and catalysts, which results its expansion as a versatile polymeric material.

Besides chemical structure, efforts have also been made to study HBPU focusing its architectural attributes. The concept of highly branched polymer was first put forward by Berzelius in early twentieth century following an  $A_2B_2+B_3$  approach using tartaric acid ( $A_2B_2$ ) and glycerol ( $B_3$ ) as raw materials.<sup>41</sup> However, "hyperbranched" terminology was first coined by DuPont researchers, Kim and Webster in late 1980s.<sup>42,43</sup> They found that it was possible to synthesize polymer with random "branch-on-branch" topology by a single pot process. After this scientific reveal, substantial efforts have been devoted towards the development of different hyperbranched polymers. In 1993, Spindler and Frechet reported the first ever synthesis of HBPU by step-growth polymerization of  $AB_2$  type blocked isocyanate and 3,5-bis[(benzoxycarbonyl)imino]benzyl alcohol.<sup>44</sup> Since then, HBPU and its nanocomposites have been intensely explored for various applications. In 1996, Kumar and Ramakrishnan synthesized HBPU with varying spacer segments in a

single pot process.<sup>45</sup> Raju and co-workers, and Karak and his group also reported synthesis of HBPU using various commercial and bio-based raw materials.<sup>46-49</sup>

On the other hand, the environmental impacts of polymeric materials have raised concerns globally over the last few decades, which force the chemists to search out biodegradable, low VOC containing PU, and also encourage to use renewable resource based raw materials. Biodegradable nature of PU came to know years after its commercial production. It is degradable under the stimuli of various micro-organisms, *viz.* fungi, bacteria, enzyme etc. In 1968, Kaplan *et al.* found that PU is susceptible for fungal degradation.<sup>50</sup> Huang and Roby (1986) studied fungi induced biodegradability of poly(amide urethane) and reported selective biodegradation in which amorphous region being degraded faster than crystalline region.<sup>51</sup> In 1991, Kay *et al.* tested bacterial degradation of PU against sixteen different bacteria isolates.<sup>52</sup> Nakajima-Kambe *et al.* (1995) demonstrated PU degradation by a soil organism called *Comamonas acidovorans*.<sup>53</sup> Besides fungi and bacteria, certain enzymes like *ureases, proteases and esterases* have also been reported to possess capability to stipulate biodegradation of PU.<sup>54-57</sup> Like biodegradability, low carbon emission during synthesis, processing and application is another desirable environmental attribute for any polymeric material. WPU is extensively mentioned in this regard. In 1994, Hart patented water based solvent free PU coating.<sup>58</sup> Kim and Lee in 1996 studied the various properties of WPU.<sup>59</sup> Lu and Lorock (2008) used soybean oil in the synthesis of WPU bringing high eco-friendly attributes to it.<sup>60</sup>

Again, the potentiality of vegetable oils in industrial utilization was first presented by J.G. Kane who is known as the father of vegetable oil based polymer.<sup>61</sup> Over the last twenty years, serious stress has been given in the development of bio-based PU. In 1984, Petrović and Fajnik reported the synthesis of castor oil based PU.<sup>62</sup> Zlatanic' *et al.* (2004) synthesized bio-based PU using 4,4-diphenylmethane diisocyanate and polyols based on sunflower, canola, soybean, corn and linseed oils.<sup>63</sup> Dutta *et al.* (2009) reported vegetable oil based PUNC with enhanced biodegradability and biocompatibility.<sup>64</sup> In this regard, naturally available polyphenolic compounds hold great promises towards the development of sustainable PU. Recently, Peng *et al.* (2013) synthesized polyphenol-based PU using hydrolysable tannins.<sup>65</sup>

In the recent past, nanotechnology based modification of polymeric materials achieved tremendous interest. State of literature reveals that fabrication of first polymer nanocomposite was carried out in 1980's by automobile giant Toyota. The work was on polyamide nanocomposite.<sup>66</sup> In 1988, Wang and Pinnavaia reported the first PUNC using clay as nano-filler.<sup>67</sup> A large number of nanomaterials of both organic and inorganic family have been utilized thereafter in the development of novel PUNCs. Kuan *et al.* (2005) reported WPU/CNT nanocomposite with enhanced mechanical, thermal and rheological properties.<sup>68</sup> Kim *et al.* (2010) prepared PU/graphene nanocomposite for the improvement of electrical and gas barrier properties.<sup>69</sup> These PUNCs are used for a wide range of applications. Thakur *et al.* (2014) reported PU/graphene as stimuli responsive self-healing and shape memory material.<sup>70</sup> Zhang *et al.* (2007) demonstrated electromagnetic shielding effect of PU/MWCNT based PUNC.<sup>71</sup> PU/HAp based nanocomposites are extensively used in biomedical applications, especially in bone tissue engineering.<sup>72</sup> Kalita and Karak (2013) developed PUNC/Fe<sub>3</sub>O<sub>4</sub> as shape memory material.<sup>73</sup> However, art of literature demonstrates only a few CD based PUNCs prior to this study. **Table 1.1.** summarizes a brief account on bio-based, environmentally benign PU based systems for various applications.

**Table 1.1.** Properties and applications of some bio-based PU, HBPU, WPU and PUNC

Type	Bio-component	Unique features/applications	Ref
PU	Soybean oil	Rigid PU foam with improved thermo-oxidative properties	74
PU	Lignin	Robust PU system with 75% renewable carbon	25
PU	Rapeseed oil	High renewable carbon content, possesses properties comparable to those with commercially available ones	75
WPU	Castor oil derived undecylenic acid as diisocyanate, castor oil based carboxylic acid type chain extender	Fully bio-based PU, high thermal properties, hydrophobic in nature	76
PU	Methyl oleate, methyl-10-undecenoate	Rigid PU, high thermal stability	77

PU	Oleic and ricinoleic acid	Eco-friendly PU with good thermal properties	78
HBPU	Castor oil	Biodegradable, used as high performance coating material	16
HBPU	Sunflower oil	Biodegradable, used as high performance coating material	17
PU	Soy-based polyol	Hydrophobic and oil resistance polymer	79
WPU	Soybean oil	Biodegradable, used as coating material	60
WPU	Starch	High mechanical properties with high water resistance	80
WPU	Chitin	High mechanical strength	81
HBPU/Nano-clay	<i>Mesua ferrea</i> L. seed oil	Cytocompatible, biodegradable	82
HBPU/Ag	<i>Mesua ferrea</i> L. seed oil	Biocompatible, antimicrobial, biodegradable	83
PU/Bentonite	Chitin	Biocompatible, non-toxic, high mechanical strength	84
HBPU/GO	Castor oil	Shape memory material	70
HBPU/Fe <sub>3</sub> O <sub>4</sub>	Sunflower oil	Biocompatible, bio-medical application	35
HBPU/MWCNT	<i>Mesua ferrea</i> L. seed oil	Biocompatible, used as shape memory biomaterial	73
PU/Cellulose nanofiber	Cellulose form palm tree	High thermal and mechanical properties	85

### 1.3. Methods and materials

#### 1.3.1. Materials

Development of polymeric nanocomposites with unique properties is desirable to meet the demands of advanced materials. In this context, PU has proved as an ideal material, since its wide spectrum of properties can be tailored by changing the structure of basic building materials. On the other hand, the nature of nanomaterial dictates the ultimate performance and application of the nanocomposite. Hence, judicious selection of raw material is noteworthy to achieve PU and its nanocomposites with desired properties. This section of the chapter makes a general review on different materials used in the preparation of PU and PUNC.



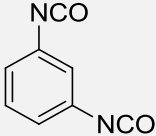
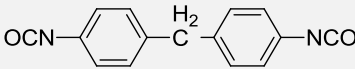
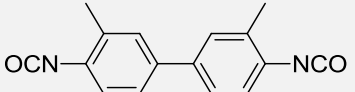
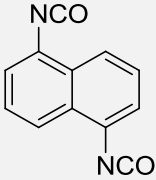
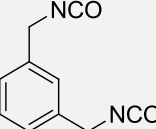
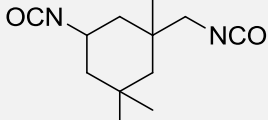
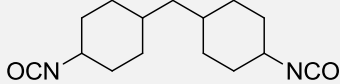
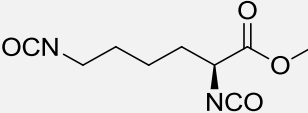
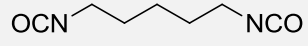
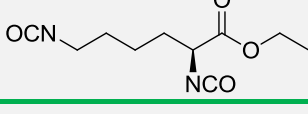
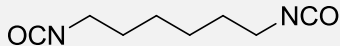
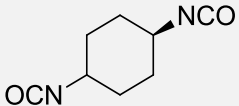
### 1.3.1.1. Polyurethane

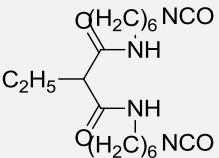
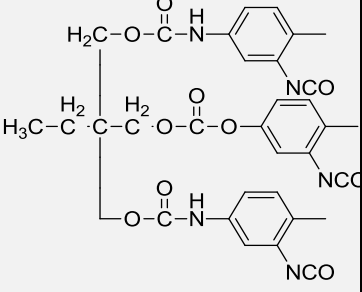
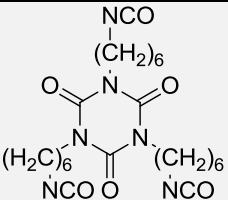
PU is a product of di/poly-isocyanate compound with di/polyols in a catalyzed or non-catalyzed reaction. Chemically, it contains polymeric backbone consisting of carbamate (-NHCOO-) linkages. However, it is possible to anchor other chemical functionalities like ester, amide, ether, urea etc. by suitably selecting the monomeric compounds. Such incorporation of chemical linkages is important to impart specific properties including biodegradability and cytocompatibility to the final product.<sup>40</sup> Synthesis of PU involves utilization of three basic components: (a) di/poly-isocyanate, (b) macroglycol and (c) chain extender. Isocyanate and chain extender together form the hard segment. On the other hand, macroglycol forms the soft segment. In recent time, stress is being given to use renewable resource based raw materials in the preparation of PU.

#### (a) Di/poly-isocyanate

Isocyanate is the one of the primary components used in PU synthesis. Wurtz in 1848 reported the first synthesis of isocyanate by alkylation of calcium cyanate and organic sulfuric acid esters.<sup>40</sup> However, the commercial importance of isocyanate was realized in 1937 when Otto Bayer introduced diisocyanate.<sup>40</sup> Currently, diisocyanates with different chemical structures are commercially available. Some commonly used diisocyanates with their structures and properties are shown in **Table 1.2**. Broadly, diisocyanates are divided into two categories, *viz.* aromatic and aliphatic. The most commonly used aromatic diisocyanates are toluene diisocyanate (TDI) and diphenyl methylene diisocyanate (MDI). TDI is generally available as a blend of 2,4- and 2,6-isomers in different proportions.<sup>86</sup> MDI is obtained in three different isomeric forms, *viz.* 4,4-, 2,4- and 2,2-MDI. O-Tolidine diisocyanate (OTDI), naphthalene diisocyanate (NDI), xylene diisocyanate (XDI) are some other aromatic diisocyanates. On the other hand, aliphatic diisocyanates include isophorone diisocyanate (IPDI), hydrogenated MDI (HMDI), 1,4-cyclohexyl diisocyanate (CHDI), 1,6-hexamethylene diisocyanate (HDI) etc. IPDI is composed of two isomers, *viz.* *cis* and *trans*.<sup>86</sup> Generally, aromatic diisocyanates are more reactive than aliphatic ones. In contrast, aromatic diisocyanates possess lower oxidation and weaker ultraviolet stabilization than aliphatic diisocyanates. Also, aliphatic isocyanates are less toxic than aromatic ones.<sup>86</sup>

**Table 1.2.** List of some important di/poly-isocyanates used in PU synthesis

Diisocyanate	Chemical structure	Unique features	Ref	
Aromatic	TDI		Used predominantly to prepare flexible PU foam, other application includes elastomers, coating, sealant etc.	86
	MDI		Used primarily to prepare rigid PU foam, high resilience foam, integral foam, coating etc.	
	O-TDI		Comparatively less reactive with H <sub>2</sub> O and air, used to prepare PU elastomers.	
	NDI		Highly reactive, used to prepare high quality tear resistance PU foam. Used to prepare only special materials.	
	<i>m</i> -XDI		Used to prepare PU elastomers.	
Aliphatic	IPDI		UV-resistant, used in the preparation of PU for coating application, also used in WPU.	86
	HMDI		Low volatile, used to prepare moisture cure and two-component PU coating.	
	L-LDI		Non-toxic, used in the preparation of PU for biomedical applications.	87
	Bio-PDI		Oleic acid derived bio-based diisocyanate, contains 70% renewable carbon.	88, 89
	ethyl ester of L-LDI		Bio-based diisocyanate, used to prepare PU based biomaterial.	
	HDI		Used to prepare PU for special coating like enamel coating, UV resistance coating etc.	86
	1,4-CHDI		Useful for the preparation of non-discoloring PU.	

Poly/di-isocyanate adduct	HDI-biuret		High molecular weight di or poly-isocyanate with low viscosity and volatility, particularly useful to obtain PU for low volatile applications such as paints, coating, adhesive etc.	90
	TDI/TMP adduct			
	HDI isocyanurate		Hydrophilic diisocyanate, used to promote aqueous dispersion of two-component PU coating system.	90

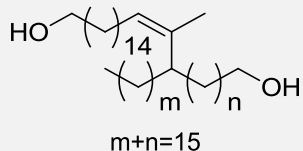
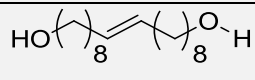
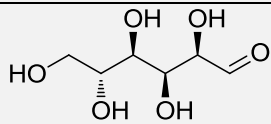
Thus, depending on the demand, these diisocyanate compounds can be suitably selected to develop PU for specific applications. To prepare special PU, high molecular weight di/poly-isocyanate adducts like HDI-biuret, HDI isocyanurate etc. have been used. This type of isocyanate is particularly useful for low volatile applications such as paints, coating, adhesive etc.<sup>90</sup> Besides commercial diisocyanates, attempt is being made to prepare bio-based ones.<sup>90</sup> L-lysine diisocyanate (L-LDI), methyl ester of L-LDI, bio-based pentamethylene diisocyanate (bio-PDI) are the examples of renewable diisocyanates.<sup>87-89</sup>

### (b) Macroglycol

These are the di or polyol compounds with molecular weight in the range of 400-5000 g mol<sup>-1</sup>. Macroglycol forms the soft segments of the PU matrix. A large number of macroglycols are available. The most commonly used macroglycols are shown in **Table 1.3**. In general, macroglycols are divided into two categories: polyether based polyol and polyester based polyol. Polyether glycols are poly(propylene oxide) glycol (PPG), poly(ethylene oxide) glycol (PEG), poly(butylene oxide) glycol (PBG), poly(tetra methylene oxide) glycol (PTMG) etc. Ether based macroglycols provide almost 90% of the polyols used industrially. On the other hand, polyester polyols are obtained by step growth polymerization reaction between di/polyol and

**Table 1.3.** List of some important commercial and bio-based macroglycols used in PU synthesis

	Macroglycol	Chemical structure	Unique features	Ref
Polyether based	PEG		Highly biocompatible, m.w. lies between 400-6000 g mol <sup>-1</sup> .	86
	PPG		Viscosity lies in between 100-1000 cp, m.w. 400-4000 g mol <sup>-1</sup> .	
	PBG		Clear viscous liquid with low pour point, m.w. 250-4000 g mol <sup>-1</sup> .	
	PTMG		Used to prepare hydrolysis resistant PU elastomer, m.w. 400-4000 g mol <sup>-1</sup> .	
Polyester based	Poly(ethylene glutarate)		Used to prepare PU with high mechanical and thermal properties.	86
	Poly(ethylene adipate)			
	Poly(1,2 propylene adipate)			
	Poly(trimethylene glutarate)			
	Poly(diethylene glutarate)			
	Polycaprolactone diol			
Bio-based	Sorbitol		Carbohydrate based polyol, used in anti-corrosive PU	91
	Castor oil based polyol		Polyester based polyol. Reportedly used in PU for biomedical application, coating, shape memory application etc.	16

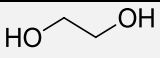
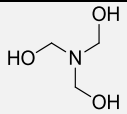
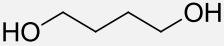
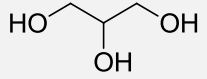
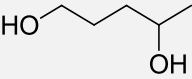
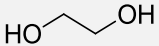
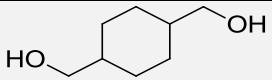
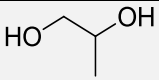
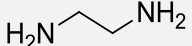
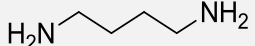
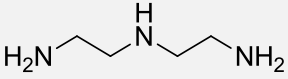
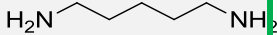
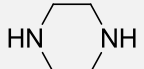
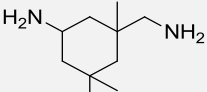
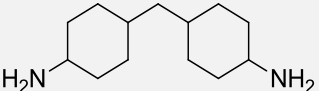
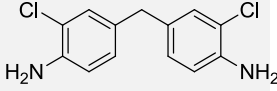
Bio-based	Oleic acid based polyol		Obtained by dimerization of oleic acid, WPU with high water resistance can be obtained.	92
	Fatty acid based diol		Linear unsaturated diol, used to prepare thermosetting PU.	93
	Glucose		Highly biocompatible, used to prepare PU based biomaterials.	94

di/poly carboxylic acids or their derivatives. For example, ethylene glycol, 1,4-butane diol, 1,6-hexane diol and a dicarboxylic acid or anhydride (aliphatic or aromatic). Generally, polyester polyols are used to obtain PU with superior mechanical strength and thermal stability.<sup>60</sup> Compared to polyether polyol based PUs, polyester polyol based PUs are more susceptible for bacterial degradation.<sup>8</sup> Here, it is pertinent to mention that macroglycol component provides huge potentiality to develop sustainable PU by utilizing a large number of bio-based hydroxyl containing compounds. In this regard, renewable resources such as vegetable oils, carbohydrates and natural polyphenolic compounds are available. Hence, it is desirable to use these bio-based macroglycols to develop eco-friendly PU.

### (c) Chain extender

These are low molecular weight (molecular weight is less than 400 g mol<sup>-1</sup>) compounds with terminal hydroxyl and amine groups. Most commonly, glycols and diamine compounds are used as chain extenders. Example includes 1,4-butanediol, 1,6-hexanediol, ethylene glycol, 1,4-cyclohexane dimethanol, ethylene diamine, diethylene diamine, isophoronediamine etc. On the other hand, multifunctional hydroxyl compounds are used in the synthesis of HBPU, e.g. pentaerythritol, triehanol amine, glycerol etc. Most commonly used chain extenders are listed in **Table 1.4**. Like macroglycol segment, bio-based chain extenders are also available. Glycerol (used as hyperbranched moiety), bio-ethylene glycol, bio-propylene glycol are bio-based hydroxyl terminated chain extenders.<sup>91</sup> On the other hand, putrescine and cadaverine are the examples of amine terminated bio-based chain extender.<sup>95,96</sup>

**Table 1.4.** List of some important chain extenders used in PU synthesis

Chain extender		Chemical structure	Chain extender	Chemical structure
Glycols	Ethylene glycol		Triethanol amine	
	1,4-Butane diol		Glycerol	
	1,3-Butane diol		Bio-ethylene glycol	
	1,4-Cyclohexane dimethanol		Bio-propylene glycol	
Amines	Ethylene Diamine		Putrescine (bio butane-1,4 diamine)	
	Diethylene triamine		Cadaverine (bio pentane-1,5-diamine)	
	Diethylene diamine		Isophoronediamine	
	4,4'-Methylene bis(cyclohexylamine)		4,4'-Methylene bis(ortho-chloro aniline)	

(d) *Catalyst*

Generally, urethane reaction is feasible even in absence of catalyst. However, in order to perform PU reaction at a low temperature and at a rapid rate catalysts are frequently used. Of particular, use of catalyst is very important for low reactive aliphatic diisocyanates. Different types of catalysts are available for urethane reaction as shown in **Table 1.5**. Most common catalysts are tertiary amines and organo-tin compounds. It is known that both types of catalysts follow different catalytic routes.<sup>97</sup> Thus, selectivity of PU reaction depends on the nature of the catalyst used. Most frequently used catalysts are 1,4-diazabicyclo[2,2,2]octane (DABCO), triethylamine (TEA), dibutyltin dilaurate (DBTDL), stannous octoate and THORCAT. Besides organo-tin compounds, organo-lead, tin, bismuth and zinc compounds also possess significant catalytic activity.

**Table 1.5.** List of some important PU catalysts

	Catalyst	Chemical structure	Mode of action	Ref
Organo-metallic	DBTDL		These catalysts activate both polyol and isocyanate. Initially, a binary complex is formed between the catalyst and polyol. It is followed by formation of ternary or bridging complex with the isocyanate. Generally, Sn based catalyst is used in rigid PU preparation as Sn salt promotes oxidative degradation in flexible PU. DBTDL catalyses IPDI based PU reaction selectively with preferential activation at 2°-NCO group.	97, 98
	Stannous octoate			
	THORCAT			
	Tetravalent tin compounds	$R_nSnX_{(4-n)}$ R=alkyl, aryl groups and X=halogen or carboxylate		
Tertiary amine	Triethylamine		Catalytic activity of amines relies on the lone pair of electron on N atom and its availability to form complexation. Generally, steric hindrance near N atom reduces catalytic activity. Electronic effect which enhances electron density at the N atom increases catalytic activity. DABCO exhibits selectivity in PU reaction, which catalyses IPDI based reactions preferentially at 1°-NCO group.	97, 98
	Dimethylcyclohexylamine			
	Dimethylethanolamine			
	DABCO			
	2-(4-Methylpiperazin-1-yl)-ethylamine			

Unlike conventional solvent borne PU, WPU builds up with four basic components, *viz.* diisocyanate, macroglycol, chain extender and internal emulsifier.<sup>26</sup> The first three components are similar to those used in conventional PU synthesis as mentioned above. The fourth component, i.e. internal emulsifier is additionally used

in WPU synthesis. These are ionogenic compounds, most frequently dihydroxyl acids which have the ability to generate ions in aqueous medium. 2,2-bis(hydroxymethyl)propionic acid (BMPA) is an example of such compound, which is frequently used in WPU synthesis.

### **1.3.1.2. Nanomaterial**

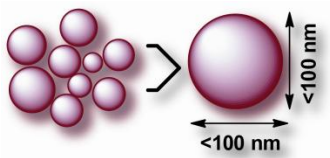
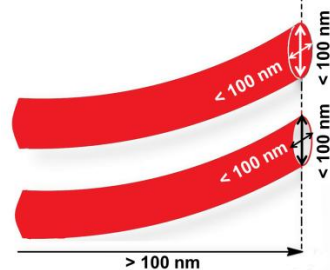
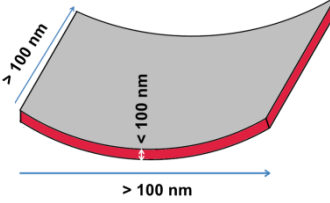
These are the materials of organic or inorganic origin, which possess at least one dimension less than 100 nm.<sup>1,34</sup> Depending on the dimensional magnitude, nanomaterials are classified into three categories, viz. zero dimensional (0-D), one dimensional (1-D) and two dimensional (2-D) nanomaterials.<sup>1</sup> Zero dimensional nanomaterial has all the three dimensions in nano scale range. Nanoparticle, nanocluster and nanocrystal fall within this category; e.g. quantum dot, metal, metal oxide based nanomaterials etc. One dimensional nanomaterial possesses two dimensions in nano range, while third dimension lies in between several hundred nanometers to micrometer range. Nanorod, nanospindle, nanofiber, nanowire, nano tube etc. belong to the one dimensional nanomaterial family. Example includes carbon nanotube (CNT), cellulose nanofiber, polyaniline nanofiber (PANI) etc. Two dimensional nanomaterial has only one dimension in nano scale regime, other two dimensions vary in between several hundred nanometers to micrometer range. This type of nanomaterial forms plate or lamellar like structure in which thickness lies within the nanoscale range, e.g. graphene based nanomaterials (GO, rGO etc.), layered silicates etc. Classification of some important nanomaterials is depicted in **Table 1.6**. All three types of nanomaterials are used in the preparation of PUNC. The choice of nanomaterial depends on the desired properties and targeted applications. On the other hand, depending on the elemental composition, nanomaterials can be classified into three classes: (a) organic, (b) inorganic and (c) hybrid (with both organic and inorganic components) nanomaterials. A brief description of these nanomaterials is provided below.

#### *(a) Organic nanomaterial*

These are primarily carbon based nanomaterials. These are the most highlighted nanomaterials in recent time because of their tunable physical, chemical, electrical, and biological properties. The most important members are graphitic nanostructures,



**Table 1.6.** Classification of some important nanomaterials according to dimensional magnitude

Type	Nano-material	Unique property
0-D 	Ag	Antimicrobial activity
	Fe <sub>3</sub> O <sub>4</sub>	Magnetic property
	TiO <sub>2</sub>	Photocatalytic activity
	HAp	Osteogenic activity
	CD	Optical property, nontoxic, sustainable synthesis
	CdS	Photo-activity
1-D 	MWCNT	Excellent electrical property
	Cellulose fibre	Sustainable synthesis, biomedical application
	TiO <sub>2</sub> nano fibre	Photo-activity
	TiN nano fibre	Optical property
	Boron nitride nanotube	Excellent electrical property
2-D 	Graphene	Excellent electrical property
	Transition metal dichalcogenide (TMDC) monolayers	Semiconductor of MX <sub>2</sub> type where M=Mo, W etc. and X=S, Se or Te.
	Silicate clays	Mechanical property
	Graphitic-C-nitride	Photocatalytic activity
	Transition metal oxide (TMO) nano-sheet	Excellent optical property, used in LED

such as GO, rGO, CNT and recently included CD. Graphene is a monolayer (2-D) of  $sp^2$  hybridized carbon atoms, which are arranged to form a honeycomb structure. Graphene possesses unique properties like high elastic modulus, large theoretical specific surface area, excellent strength, high thermal and electrical conductivity etc.<sup>99</sup> These attributes make graphene attractive as a candidate to fabricate PUNC. CNT is a cylindrical (1-D) type nanomaterial and possesses unique length to diameter ratio, which may extent up to 132,000,000:1.<sup>100</sup> CNT exhibits extraordinary mechanical and electrical properties as well as thermal conductivity by virtue of which it finds extensive application as a nano-filler in various polymeric materials. On the other hand, CD is the youngest member in the family with unique dimension, which is less than 10 nm (0-D). CD exhibits excellent nano state aqueous solubility, exciting optical properties and profound biocompatibility.<sup>101</sup> Most importantly, CD

provides facile preparative route by using nontoxic chemicals, environmentally benign solvents and renewable carbon based precursors. Nowadays, CD is used to develop polymeric nanocomposites for optical, biological and photocatalytic applications. Besides these, cellulose, PANi nanofiber etc. also belong to organic nanomaterial family.

#### (b) *Inorganic nanomaterials*

Inorganic nanomaterials include different metals, metal oxides, metal chalcogenides, metal pnictides, inorganic minerals and nano clays. Reduction of metal salts in presence of capping agents provides the most common route to obtain metal nanocrystals like silver (Ag), gold (Au), rhodium (Rh), iridium (Ir), platinum (Pt) etc.<sup>34</sup> Nano metal oxides are obtained by solvolysis, wet chemical, sol-gel or hydrolysis method using organometallic precursors.<sup>34</sup> Iron oxide ( $\text{Fe}_3\text{O}_4$ ), copper oxide ( $\text{Cu}_2\text{O}$ ), manganese oxide ( $\text{Mn}_3\text{O}_4$ ), rhenium oxide ( $\text{ReO}_3$ ), zinc oxide (ZnO), metal ferrites ( $\text{MFe}_2\text{O}_4$ , M=Fe, Co or Zn) etc. are the examples of metal oxide nanocrystals. Nanocrystals of metal chalcogenides are generally prepared by the reaction of metal salts with an appropriate sulfiding or seleniding agent under solvo-thermal condition.<sup>34</sup> Example includes cadmium chalcogenide nanocrystals (CdE, where E=S, Se, Te). On the other hand, HAp is an example of nanomaterial belonging to inorganic minerals. This nanomaterial possesses excellent biocompatibility with osteogenic activity, hence frequently used to design PUNC based polymeric scaffold or prosthesis for bone tissue engineering applications.<sup>72</sup> Nanoclays are hydrous aluminum phyllosilicate thin platelets or sheets having layered structure in the nanometer scale.<sup>102</sup> The most commonly used nanoclays are montmorillonite (MMT), hectorite, saponite etc.

#### (c) *Hybrid nanomaterials*

Besides organic and inorganic nanomaterials, a new class of nanostructures has recently attracted the researchers. Such type of nanomaterials consists of two or more different types of nanomaterials interacting with each other through a definite mechanism within the same system.<sup>39</sup> Such systems may contain both organic and inorganic components and possess unique advantages over the individual ones. Depending on the interaction between the nanocomponents, different types of morphology can be achieved, e.g. decorated nanohybrid, embedded nanohybrid etc.



terminated pre-polymer is formed by the reaction between diisocyanate and macroglycol.<sup>105</sup> Chain extension of this pre-polymer is carried out in the second step to obtain the final polymer. Generally, one-shot process is rapid and it is difficult to control the reaction, especially when multifunctional chain extender is used.<sup>105</sup> In contrary, pre-polymerization technique is more reliable, reproducible, precise and it offers more variables to control the reaction. This method is particularly useful for the synthesis of HBPU in a one pot process without the risk of gelation and with high degree of branching. Monomeric systems like  $A_2+B_3$ ,  $A_2+B_4$ ,  $A_2+CB_2$ ,  $A_2+C_2B_2$  etc. are readily used to produce HBPU by pre-polymerization technique.

Different solvents are also used in PU synthesis to control the reaction. Most commonly used solvents are xylene, dimethylacetamide (DMAc), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) etc. However, the environmental concern regarding high VOC content of such solvent borne PUs has forced the material scientists to find out eco-friendly alternatives. As a result WPU has emerged out, which contains PU macro-particles dispersed in an aqueous phase. WPU synthesis follows the pre-polymerization technique. Synthesis of WPU involves use of four different components.<sup>98</sup> These are diisocyanate, macroglycol, chain extender and internal emulsifier. The fourth component usually consists of a dihydroxyl acid, which generates ions when treated with tertiary amine. Generally, first step is carried out without using any solvent. Internal emulsifier is incorporated to the PU chain at this step. In the second step, water miscible organic solvent having boiling point less than 100 °C (practically it should be less than 85 °C) is used. After the completion of the reaction ions are generated along the polymer backbone by treating with tertiary amine. Then water is added at a very slow rate. Chain extension can also be performed at this step by using diamine chain extender. Finally, organic solvent is removed under reduced pressure to obtain the aqueous solution of PU.

### **1.3.2.2. Nanomaterial preparation**

Preparative methods of nanomaterial consist of two major approaches, *viz.* (a) top to bottom and (b) bottom to top.<sup>106</sup> In a top to bottom approach, nanomaterial is formed by breaking down of a larger structure (bulk precursor material) into nano sized structure. Generally, harsh and drastic conditions are employed in this approach. Various methods have been utilized in the “breaking down” process. These include

ball milling, mechano-chemical processing, arc discharge, laser ablation, electro-chemical method etc. On the other hand, bottom to top approach of synthesis relies on the use of precursors in the molecular level, which aggregate through polymerization, condensation or pyrolysis to form nano structured materials. Various methods have been employed under this approach, which include hydrothermal, microwave assisted pyrolysis, sono-chemical synthesis, co-precipitation method, sol-gel method etc. Bottom to top approach is the most commonly adopted approach compared to top to bottom method. It is less expensive, time saving and it offers large scale production. Further, bottom to top approach offers better control over the morphology and size distribution of the nanomaterial.<sup>106</sup>

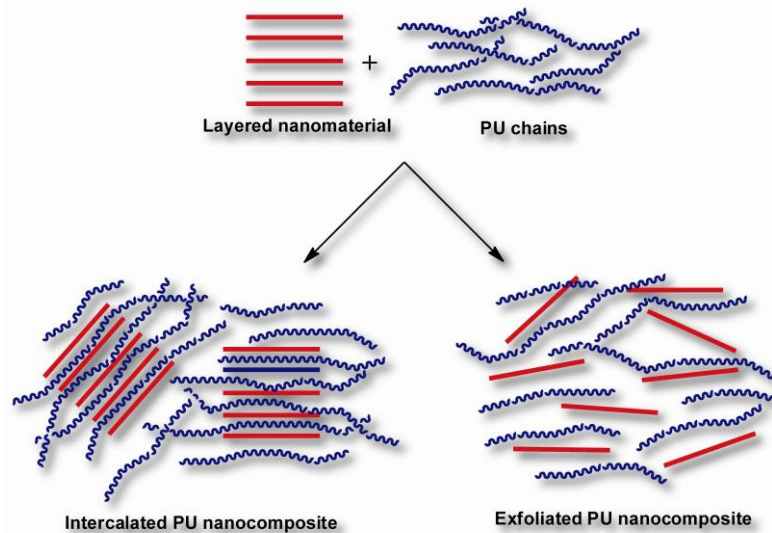
### ***1.3.2.3. Polyurethane nanocomposite fabrication***

In a polymer nanocomposite, nanomaterial is uniformly dispersed in the polymer matrix and a strong interaction exists between the nano and macro structures. Different preparative techniques have been used to fabricate polymer nanocomposite. These include solution technique, *in situ* technique, melt mixing method etc.<sup>1,107,108</sup> These are general methods and most frequently used in the fabrication of PUNC. A brief description of these methods is provided below.

#### *(a) Solution technique*

Solution technique involves use of a suitable solvent or mixture of solvents to swell and disperse the nanomaterial. The nanomaterial in dispersed phase is then incorporated to the PU matrix by using shearing mechanical force followed by ultrasonication. Finally, nanocomposite is obtained by evaporating the solvent. Generally, interactions between nanomaterial-solvent, polymer-solvent and nanomaterial-polymer dictate the final state of nanomaterial dispersion in the polymer matrix.<sup>107,108</sup> When nanomaterial-solvent interaction dominates over the others, then nanomaterial disintegrates in an adequate amount of solvent. On contrary, if polymer-nanomaterial interaction is strong enough, polymer chains penetrate into the nanomaterial and absorbed onto their surface, thereby forming an exfoliated nanocomposite. Such exfoliated state becomes stable even after the removal of the solvent. However in most of the cases, nanomaterial-polymer interaction is not strong enough, which results ready accessibility of solvent molecules to the nanomaterial. Hence, after removal of the solvent nanoparticles tend to form small

aggregates with the polymer chains sandwiched in between them. This results in the formation of well-ordered intercalated nanocomposite (**Figure 1.1**). However, this technique associates with certain disadvantages, e.g. high cost due to the use of solvent, concern regarding health and environmental hazards, low level of interaction etc. But, the method is useful when water is used as solvent.



**Figure 1.1.** Schematic presentation of intercalated and exfoliated PUNC.

(b) *In situ* polymerization

In *in situ* polymerization technique, nanomaterial is swollen and dispersed into the monomeric precursors or pre-polymer, which are then subjected to polymerization reaction to obtain polymeric nanocomposite. Compared to solution technique, the level of interaction between polymer and nanomaterial is very high as viscosity of monomeric precursors or pre-polymer is less compared to the respective polymer. This results in easy accessibility of the nano and macro structures within the system. *In situ* polymerization often forms exfoliated polymer nanocomposite (**Figure 1.1**).<sup>1,107,108</sup> Since nanomaterial is added well before the polymerization reaction, hence, it can take part in the reaction or cross-linking process and thus influence the ultimate properties of the nanocomposite. In case of PUNC, nanomaterial is generally swollen and dispersed after the pre-polymerization step. The main advantage of *in situ* polymerization is strong polymer-nanomaterial interaction without using additional solvent.

### (c) *Melt mixing technique*

Melt mixing technique involves direct mixing of the nanomaterial with the pristine polymer in the molten state by using suitable mixing and processing equipments like twin screw mixers, rollers, injection molding etc. In melt mixing process, amorphous polymers are generally processed above their glass transition temperature and semi-crystalline polymers are processed above their melting temperature. Generally, the melt viscosity of polymer is very high. This causes poor intercalation of the nanomaterial as compared to *in situ* technique. Hence, only partially exfoliated structure can be obtained by this method. However, from environmental point of view this method is safe, as no solvent is required in the fabrication of the nanocomposite.<sup>1</sup> Further, this method can be used for commercial scale production of polymer nanocomposite.

Besides these techniques, polymer nanocomposites are also fabricated by few other techniques such as coagulation spinning, solid-state mechano-chemical or twin-screw pulverization processes, template synthesis, latex fabrication, sol-gel process, thermal decomposition, plasma treatment etc.<sup>107,108</sup>

## **1.4. Characterization**

Different analytical, spectroscopic, microscopic and visual techniques are used for structural characterization of HBPU, nanomaterial and PUNC. These methods are briefly summarized below.

### **1.4.1. Spectroscopic techniques**

#### **1.4.1.1. UV-visible**

This is one of the most commonly used spectroscopic techniques. Functional groups which exhibit absorption in the UV-visible region due to  $n-\pi^*$  and  $\pi-\pi^*$  transitions can be detected by this technique. UV-visible technique is particularly useful for the characterization of metallic nanomaterials and their nanocomposites. Every metal nanoparticle possesses characteristic surface plasmon resonance value.<sup>108,109</sup> The position and shape of surface plasmon resonance depend on the size, shape of the particles and dielectric constant of the medium. Generally, plasmon oscillation damps when particle size is significantly smaller than the mean path length of electrons in bulk metal. Thus, red shift in the plasmon resonance absorption of a nanomaterial



occurs, which indicates formation of agglomeration. On the other hand, blue shift indicates reduction in size of nanomaterial. A sharp absorption is indicative of a narrow size distribution.<sup>108,109</sup> Further, UV-visible spectroscopic technique is quite helpful to determine band gap of nanomaterials, especially those of semi-conductor based quantum dots. This technique can also be used to quantify transparency of PUNC film in terms of percentage transmittance.

#### **1.4.1.2. Fourier Transform Infrared (FTIR)**

FTIR spectroscopy is used to detect various functional groups present in HBPU, nanomaterial and PUNC. The most significant FTIR bands for PU are carbonyl stretching ( $\text{-C=O}$ ) vibration near  $1630\text{--}1750\text{ cm}^{-1}$  region (amide-I) and amine ( $\text{-N-H}$ ) stretching vibration near  $3400\text{--}3500\text{ cm}^{-1}$  region. Appearance of these two bands furnishes evidence for the formation of urethane ( $\text{-NHCOO-}$ ) linkage. FTIR technique is also helpful for the study of H-bonding that exists within HBPU structure. Generally, formation of hydrogen bonding can be identified by following the shift of amide-I and  $\text{-N-H}$  bands towards lower wavenumber region.<sup>110</sup> A broad FTIR band also indicates existence of H-bonding. Similarly, different nanomaterials possess characteristics IR frequencies from which they can be identified.

#### **1.4.1.3. Nuclear Magnetic Resonance (NMR)**

NMR spectroscopy is frequently used for the structural characterization of HBPU. Especially, different proton and carbon environments present in HBPU are easily identified by this technique (using  $^1\text{H}$  and  $^{13}\text{C}$  NMR). In certain cases, NMR is used to confirm the formation of isomeric urethane linkages, e.g. in IPDI based PU, formation of two isomeric di-urethanes ( $Z$  or  $E$ ) can be confirmed by  $^1\text{H}$ -NMR spectroscopy.<sup>111</sup> NMR is also a very useful tool for studying the architectural feature of HBPU. Careful analysis of NMR spectrum allows estimation of degree of branching of the hyperbranched structure.<sup>112</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR are also useful in the structural study of carbon based nanomaterials and polymeric nanocomposites. Recently, De *et al.* (2015) showed its utility in the structural characterization of CD and hyperbranched epoxy/CD nanocomposite system.<sup>113</sup>



## 1.4.2. Scattering techniques

### 1.4.2.1. X-Ray Diffraction (XRD)

XRD can be used for the determination of degree of crystallinity or amorphousness of polymeric materials.<sup>108</sup> This technique is particularly useful for the study of nanomaterial. It reveals valuable information regarding crystallinity and crystal structure of nanomaterial. From the diffraction angles ( $2\theta$  values), intensity and shape of diffraction peaks, it is possible to identify various diffraction planes. XRD technique also offers the scope to determine the inter-layer spacing in a nanostructure, which is calculated by using Bragg's equation as shown below.

$$n\lambda=2d\sin\theta\text{.....(Eq.1.1)}$$

where,  $n$  is order of diffraction,  $\lambda$  is wavelength of X-ray,  $\theta$  is diffraction angle and  $d$  is inter-planar distance. Shift of diffraction peak towards lower diffraction angle indicates increase in interlayer distance. This often arises as a result of intercalation of polymer chains in between the layers of nanomaterial after the formation of polymeric nanocomposite. Hence, by observing position of diffraction peaks it is possible to obtain ideas about the nature of interactions between PU and nanomaterial within the matrix.

### 1.4.2.2. Raman scattering

Raman scattering is often used to gather vibrational information, especially for carbon based nanomaterials including GO, rGO, CNT, CD etc.<sup>114</sup> The fingerprint provided by Raman is helpful for structural characterization of these nanomaterials. Raman spectrum of allotropic carbon nanomaterials always displays G band (near  $1575\text{ cm}^{-1}$ ), which represents  $sp^2$  hybridized graphitic carbon structure. On the other hand, D band (near  $1350\text{ cm}^{-1}$ ) indicates the presence of disorder in the graphitic structure. There may appear another band, i.e. 2G (near  $2800\text{ cm}^{-1}$ ) which is indicative of layered carbon nano-structure. The relative intensities of D and G bands (in terms of  $I_D/I_G$  ratio) furnish information about the extent of disorder. High value of  $I_D/I_G$  ratio designates high level of disorder. Raman analysis is also helpful for certain metallic nanomaterials as well. For example, nano HAp exhibits a peak at

wavenumber  $954\text{ cm}^{-1}$  corresponding to symmetric stretching mode vibration of  $\text{PO}_4^{3-}$ .<sup>115</sup>

### **1.4.3. Microscopic techniques**

#### ***1.4.3.1. Scanning Electron Microscopy (SEM)***

This is a visual microscopic technique which reveals valuable information regarding surface topology of PU, nanomaterial and PUNC. SEM images are obtained by scanning of a sample with a focus beam of high energy electrons. This results generation of a variety of signals at the surface of the sample under scanned, which contain valuable information about the external morphology and chemical composition of the specimen. This technique can be used to study the presence of inhomogeneity and crystallinity within a polymer matrix.<sup>108</sup> On the other hand, surface morphology of nanomaterial including size and shape can be studied with the help of SEM analysis. SEM also provides visual information about the distribution and orientation of the nanomaterial in PUNC matrix.<sup>108</sup> SEM in conjugation with Electron Dispersive X-ray (EDX) technique is useful for the elemental analysis of PU and nanomaterials.

#### ***1.4.3.2. Transmission Electron Microscopy (TEM)***

TEM is the most important tool for the study of internal structure of nanomaterial and its distribution in PUNC.<sup>108,116</sup> TEM uses high energy electron beam, which is passed through a ultra-thin film of the specimen. This causes interaction of the electron beam with the sample. The transmitted electrons coming out of the sample carry valuable information about the internal structure of the specimen. TEM images of nanomaterial are very useful, which furnish information about its size, shape and size distribution. High Resolution TEM (HRTEM) image provides information about inter-planar distance within a nanostructure.<sup>116</sup> Selected Area Electron Diffraction (SAED) pattern provides evidence about the crystallinity and crystal structure of a nanomaterial. Fast Fourier Transform (FFT) and Inverse Fast Fourier Transform (IFFT) images are also helpful in this regard. TEM is also used to study chemical composition of a nanomaterial by using EDX technique. TEM provides visual evidence, which depicts the exact distribution of nanomaterial in a PUNC matrix.

## 1.5. Testing methods

### 1.5.1. Mechanical

Evaluation of various mechanical properties like tensile strength, tensile modulus and elongation at break values involves use of Universal Testing Machine (UTM). Standard testing protocol ASTM D882-12 is generally adopted for the measurement of tensile strength using rectangular film samples of HBPU and PUNC.<sup>117</sup> On the other hand, impact resistance can be measured by using an impact tester following standard ASTM D1037-16a falling weight method.<sup>118</sup> ASTM D7027-13 standard protocol is used for the measurement of scratch resistance of thin polymeric coating.<sup>119</sup>

### 1.5.2. Thermal

Thermal properties including determination of thermal degradation pattern, onset of degradation, end set of degradation etc. are evaluated with the help of Thermogravimetric Analyzer (TGA).<sup>107,108</sup> TGA provides these data in terms of change in weight as a function of temperature. First derivative of TG curve (DTG) gives rate of weight loss at a particular temperature. On the other hand, Dynamic Scanning Calorimetry (DSC) can be used to study thermal transition behavior of polymeric material.<sup>1</sup> DSC is helpful to determine glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of PU and PUNC. TGA and DSC can also be used for the study of thermal degradation kinetics and cross-linking kinetics, respectively.

### 1.5.3. Chemical

Chemical resistance test of PU and PUNC is carried out under different chemical environments (which may be acidic, alkaline or saline) in order to judge their resistance towards different chemicals. Standard method in accordance with ASTM D543-14 is generally adopted for the study of chemical resistance of polymeric materials.<sup>120</sup>

## 1.5.4. Optical

### 1.5.4.1. Transparency

Transparency is a very important optical property for any polymeric material. It is quantitatively measured by determining percentage of light transmitted through a polymeric film. Practically, it is performed by measuring the absorbance with the help of a UV-visible spectrometer in the visible region 400-700 nm. Absorbance (A) values are then converted into percentage of transmittance (%T) by using the following equation.<sup>121</sup>

$$A=2-\log_{10} \%T\text{.....(Eq.1.2)}$$

### 1.5.4.2. Photoluminescence

Quantum dots and quantum dot based polymeric nanocomposites exhibit especial optical properties like photoluminescence (PL).<sup>121</sup> The exact behavior of PL can be studied by taking spectrum in a PL spectrometer. This technique uses the light from an excitation source to pass through a filter or monochromator which strikes the sample. A proportion of the incident light is absorbed by the sample and some of the molecules undergo fluorescence. The fluorescent light is emitted in all directions. Some of this fluorescent light passes through a second filter or monochromator and reaches a detector, which is usually placed at 90° to the incident light. Various light sources may be used as excitation sources, which include lasers, LED, xenon arcs, mercury-vapor lamps etc. Unusual PL behavior like up-conversion can also be studied with the help of PL spectroscopy.

## 1.5.5. Biological

### 1.5.5.1. Cell viability

MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] assay is one of the most widely adopted methods to test the viability of nanomaterial, PU and PUNC with any mammalian cell.<sup>122</sup> The method is based on the fact that yellow coloured 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide undergoes reduction to purple coloured insoluble 3-(4,5-dimethylthiazol-2-yl)-1,3-diphenylformazan (commonly known as formazan) under the action of mitochondrial reductase in living

cells. The extent of reduction reflects the viability of the cells, which can be quantified by calorimetric method. In real practice, formazan is dissolved in a solvent (generally dimethyl sulfoxide, acidified ethanol or sodium dodecyl sulphate diluted with hydrochloric acid) and absorbance is measured at wavelength of 500-600 nm. The value of absorbance is directly proportional to the number of viable cells which indicates cell viability.

#### **1.5.5.2. Cell proliferation**

Alamar Blue assay is one of the most commonly used methods for cell proliferation study.<sup>123</sup> It offers a simple, rapid and sensitive measurement for the estimation of viability of mammalian cells. Alamar Blue contains weakly fluorescent, non-toxic dye called resazurin. This dye acts as a redox indicator and undergoes calorimetric changes under the stimuli of cellular metabolic reduction. The reduced form of resazurin is called resofurin, which is highly fluorescent compound. Intensity of fluorescence is directly proportional to the number of living cells. Hence by measuring absorption of resofurin (at wavelength 500-600 nm), it is possible to quantify the rate of cell proliferation over a period of time.

#### **1.5.5.3. Biodegradation**

Standard method like ASTM D6691-09 is used for the study of biodegradation.<sup>124</sup> In such method bacterial culture is maintained in a medium consisting of  $(\text{NH}_4)_2\text{SO}_4$  (2.0 g),  $\text{Na}_2\text{HPO}_4$  (2.0 g),  $\text{KH}_2\text{PO}_4$  (4.75 g),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (1.2 g),  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (0.5 mg),  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  (100 mg),  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (70 mg),  $\text{H}_3\text{BO}_3 \cdot 5\text{H}_2\text{O}$  (10 mg),  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$  (100 mg),  $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  (1 mg) and  $\text{MoO}_3$  (10 mg) in 1 L distilled  $\text{H}_2\text{O}$ . Polymeric films are kept in this medium for a definite time. The rate of biodegradation is followed by measuring change in weight and calorimetric estimation of bacterial growth at regular intervals of time.

### **1.6. Properties**

As discussed in the introductory section, the primary objective of formation of PUNC is to improve the inferior properties of the pristine system without deteriorating the superior ones. Nature and extent of improvement depend on the properties of the nanomaterial used and interfacial interaction exist between polymer matrix with the

nanomaterial. This section briefly describes general properties PU and improvement of these properties by the formation of nanocomposite.

### **1.6.1. Physical**

Physical properties of PU include solubility, viscosity, molecular weight etc. Conventional solvent borne PUs are soluble in polar organic solvents like xylene, acetone, THF, DMSO, DMAc etc. Extent of solubility depends on molecular weight and polarity of the solvent used. PU is insoluble in aqueous medium and alcohols. However, it is possible to obtain aqueous PU dispersion by incorporating a suitable emulsifier into the polymer backbone.<sup>30,59</sup> Generally, fabrication of nanocomposite does not interfere the solubility parameters of the pristine system. However, architectural features of PU seem to influence these physical properties significantly. HBPU is more soluble than linear analogous PU. Likewise, HBPU possesses significantly low solution viscosity compared to its linear counterpart even with a high molecular weight.<sup>1,27</sup> With increase in degree of branching, solution viscosity tends to decrease. Upon formation of PUNC, solution viscosity generally increases depending upon the nature of nanomaterial used. Clay based nanomaterials are known to increase solution viscosity. On the other hand, HBPU has very narrow molecular weight distribution, which tends to approach unity with increase in branching.<sup>112</sup>

### **1.6.2. Mechanical**

Mechanical properties include tensile strength, elongation at break, elastic modulus, toughness, scratch hardness, impact resistance etc. It is known that incorporation of even small amount of nanomaterial (>5 wt%) into a PU matrix enhances most of these properties significantly. In most of the cases, tensile strength increases upon formation of nanocomposite and this enhancement is dose dependent. The extent of enhancement depends on the distribution of nanomaterial within the polymer matrix.<sup>108</sup> Generally, well dispersed nanomaterial favors high strength, while agglomeration tends to reduce the same. Similarly, exfoliated nanocomposite exhibits better strength improvement compared to intercalated ones. On the contrary, flexibility and elongation at break values tend to decrease after the formation of nanocomposite. However, it does depend on the nature of the nanomaterial used. In

recent time, CD has been shown as a superior nanomaterial with enhanced flexibility in a hyperbranched epoxy/CD nanocomposite.<sup>121</sup> Other mechanical properties like elastic modulus, scratch hardness, impact resistance etc. are often found to be increased upon formation of PUNC. On the other hand, toughness depends on the extent of enhancement in tensile strength and consequent reduction in elongation. If magnitude of increase in tensile strength exceeds that of reduction in elongation, then overall gain in toughness can be achieved. Most of the reported PUNCs, like PU/Fe<sub>2</sub>O<sub>3</sub>, PU/rGO, PU/HAp, PU/MWCNT etc. demonstrate overall gain in mechanical performance compared to their pristine form.<sup>35,70,73,125</sup>

### 1.6.3. Thermal

Thermal properties include thermal degradation stability, thermal transition behavior, flame retardancy etc. It has been found that formation of PUNC is always accompanied by enhancement in thermal properties. Metallic nanomaterials often create a barrier against the volatile decomposed product from escaping. This slows down the decomposition process, which ultimately imparts better thermal stability.<sup>126</sup> Despite of poor thermal resistance, carbon based nanomaterials like GO, rGO, MWCNT etc. are also found effective for the enhanced thermal stability of PUNC. They form char which act as thermal insulator and hence slows down the rate of degradation.<sup>127</sup> Thermal transition behavior of PUNC is another important aspect, which can be studied by measuring  $T_g$  and  $T_m$ . Generally, both  $T_g$  and  $T_m$  increase upon formation of nanocomposite. It is due to increase in rigidity of the system imparted by nanomaterial, which restricts the molecular chain orientation within the matrix. Thakur and Karak (2014) recorded a positive shift in  $T_g$  (from -20 to -15 °C) and  $T_m$  (from 38 °C to 41 °C) by incorporating GO into a HBPU.<sup>70</sup> Similar shift was also observed by Kalita *et al.* (2014) in a HBPU/MWCNT nanocomposite.<sup>128</sup> Likewise, flame retardancy of pristine PU can be improved by preparing nanocomposite. Metallic nanomaterials are particularly useful in this regard.

### 1.6.4. Optical

General optical properties of PUNC include color, gloss, transparency etc. It is always a matter of interest to retain the original color and transparency of the neat polymer after the formation of nanocomposite. In most of the PUNC, transparency, color and

gloss are not affected much. This can be attributed to nano-size dimension, low level light scattering and small amount of nanomaterial loading. However, carbon based nanomaterials like GO, MWCNT etc. may cause loss of transparency as well as original color. Besides these common behaviors, PUNC may also exhibit especial optical properties like fluorescence, luminescence, non-linearity etc. Various luminescent quantum dots are the potent candidates in this regard. Cao *et al.* (2007) reported WPU/CdTe nanocomposite as a luminescent material.<sup>129</sup> Chen *et al.* (2007) used CdS quantum dot for fabrication of PU with enhanced optical properties.<sup>130</sup>

#### 1.6.5. Catalytic

This is one of the modern aspects of polymer nanocomposite which may find immense value in coming days. It is known that a large number of nanomaterials, which include metal, metal oxide, quantum dot, CD etc. possess profound catalytic activity. In particular TiO<sub>2</sub>, ZnO, semiconductor based quantum dots, CD etc. act as photo-catalyst due to their light harvesting activity. Hence, nanocomposites of these nanomaterials are also expected to exhibit catalytic activity. Recently, Hazarika and Karak (2016) reported hyperbranched polyester/CD nanocomposite, which can catalyse photo-degradation of formaldehyde and methylene blue.<sup>131</sup> Such material can be used as an eco-friendly and self-cleaning coating material. Similarly, De and Karak (2014) reported epoxy/CD nanocomposite for photo-degradation of dye.<sup>132</sup> Mosconi *et al.* (2015) used different polymer/CD nanocomposites for UV induced H<sub>2</sub> generation, photo-oxidation of bezyl alcohol and photo-reduction of Ag<sup>+</sup> into Ag<sup>0</sup> nanoparticle.<sup>133</sup>

#### 1.6.6. Electrical

Electrical properties of PU and their nanocomposites are commonly associated with the insulating or conducting behavior against flow of current. Generally, pristine PU behaves as an insulating material. However, it can be made conducting by forming nanocomposite. Nanomaterials like GO, rGO, CNT etc. possess excellent electrical conductivity.<sup>134</sup> These nanomaterials are often used to fabricate conducting PUNC. Kim *et al.* showed that incorporation of even 1 wt% of graphene based nanomaterial can make a PU matrix electrically conductive.<sup>69</sup> Likewise, Koerner *et al.* (2005) revealed that incorporation of small amount of CNT (0.5%-10 vol%) can enhance



electrical conductivity of PU up to  $\sigma \sim 10 \text{ S cm}^{-1}$ .<sup>135</sup> Literature shows that graphene allows the transition from insulator to conductor at significantly lower loading compared to CNT.

### 1.6.7. Biological

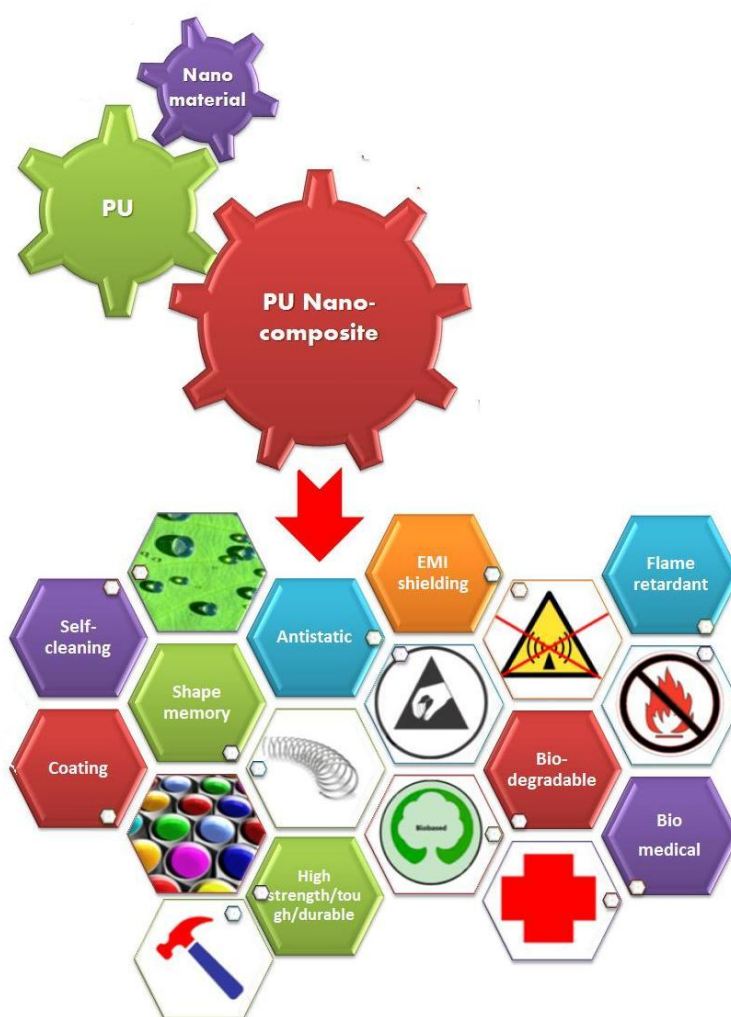
One of the most important properties of PU is its biological attributes. PU is known as a biocompatible and biodegradable polymer.<sup>136</sup> Hence, this polymer is used extensively in various biomedical applications. However, it is always a matter of interest to enhance its inherent bioactivity. Because, as a synthetic matrix, it lacks target specific bioactivity and associates with the risk of host reaction due to xenobiotic behavior. This can be achieved by the formation of PUNC by selecting suitable nanomaterial. Nanomaterials like HAp, GO, rGO, MWCNT, CD, Fe<sub>3</sub>O<sub>4</sub> etc. are reportedly used for the fabrication of PUNC based biomaterials. For example, HAp exhibits profound osteogenic activity. Hence, nanocomposite of PU/HAp is frequently used in bone tissue engineering application.<sup>73</sup> Likewise, incorporation of Ag, ZnO, TiO<sub>2</sub> etc. imparts antibacterial activity to the host polymer.<sup>137,138</sup> MWCNT and Fe<sub>3</sub>O<sub>4</sub> are known to confer wound healing ability.<sup>35,125</sup> Here, it is pertinent to mention that recent biomaterial research tries to utilize bio-functionalized nanomaterials for the fabrication of biocompatible polymers. Such functionalized nanomaterial carries bioactive motif, which may be peptide, protein, enzyme or any kind of drug molecule. Fabrication of polymeric material with such bio-nanohybrid imparts excellent target specific bioactivity. Das *et al.* (2013) fabricated PU with peptide functionalized MWCNT and used it for accelerated *in vivo* bone tissue regeneration.<sup>139</sup>

On the other hand, biodegradability is another important bio-characteristic of PU. Especially, polyester based PUs are significantly susceptible for bacterial degradation under the exposure of various micro-organisms like bacteria, fungi or enzyme. In addition to ester, other chemical linkages like amide, urea etc. are also known to enhance biodegradation process of PU. However, it is difficult to put forward a generalized idea about the impact of formation of nanocomposite on biodegradability of a polymer. Because, literature shows both enhancement and decrement in the rate of biodegradability upon formation of nanocomposite. Mishra *et al.* reported slow degradation rate after incorporation of nanoclay in PU due to

increase in the crystallinity.<sup>140</sup> However, Okamoto *et al.* (2006) reported that degradation was improved after the formation of nanocomposite based on poly(lactic acid) and trimethyl octadecylammonium modified MMT.<sup>141</sup> They postulated that hydroxyl groups heterogeneously catalyzed the hydrolysis of matrix upon water adsorption due to intercalated silicate layers. Likewise, Deka *et al.* (2010) reported enhanced biodegradability of a HBPU/MWCNT nanocomposite.<sup>142</sup> Hence, it can be said that biodegradability of PUNC depends on the nature of nanomaterial used and it is a matter of thorough study.

### 1.7. Applications

PU and PUNC have found diversified applications due to their wide range of properties (**Figure 1.2**). Some of the important applications are discussed below.



**Figure 1.2.** Wide spectrum of PU application.

### **1.7.1. Adhesive and sealant**

PU is used as adhesive and sealant.<sup>143</sup> PU adhesive is used extensively to bind nonporous surfaces like metal, wood, glass etc. One of the advantages of PU adhesive is high water and chemical resistance. On the other hand, PU sealant is used to fill up gaps to prevent air and water leakages. The most significant feature of PU sealant is its flexibility along with the advantages of moisture, chemicals and corrosion resistance. Moreover, inherent resiliency of PU provides resistance against cracking and physical forces to the joint material. Generally, PU adhesive and sealant are available in both one and two component systems. Crater (2013) recently reported PU based adhesive and sealants with improved elastomeric properties.<sup>144</sup>

### **1.7.2. Furniture and bedding**

Flexible PU foam is used in various furniture and furnishing applications, which include upholstered furniture cushions, carpet cushion, automotive seat cushions, interior trim, mattress padding, solid-core mattress cores etc.<sup>145</sup> Flexible PU foam is soft and provides good structural stability, durability and comfort. Compared to leather finished furniture, PU based furniture are cost effective and easy to care.

### **1.7.3. Building material**

PU is used to make various building materials like artificial wall, home appliances, decorative items, sculptures etc. Rigid PU foam is suitable to make wall, ceiling and roof of modern houses. PU foam is also utilized as thermal insulator.<sup>146</sup> On the other hand, PU resin can be used as an aesthetic flooring material.<sup>147</sup> Being seamless and water resistant, such polymeric floor is getting substantial interest. As building material, PU offers several advantages. These are light in weight, possess high water and chemical resistance, easy to mold into desired shape and size and easy to install. Hence, PU along with its nanocomposites are widely used to obtain different building materials.

### **1.7.4. Automotive**

PU in various forms is used in automotive industry to build various components. Flexible and semi-flexible PU foams are used in the designing of interior parts like arm rest, head rest, roof liners, dashboard etc.<sup>148</sup> Flexible PU foam is extensively used

to make automobile seats. The most significant advantages of using polymer based material over metal are light weight, low cost, corrosion resistance etc. On the other hand, compared to conventional fiber glass, it provides better durability and flexibility. In the last twenty years, PUNCs are being also used in the automotive industries for manufacturing of different structural parts such as bumpers, side skirts, roll pans and wiper cowls etc. PU/nanoclay and PU/TiO<sub>2</sub> nanocomposites are two such examples, which have been widely used by automobile manufactures.<sup>149-150</sup>

### 1.7.5. Surface coating

PU is extensively used for surface coating application. It is particularly suitable for application to surfaces, which require high level of chemical as well as physical resistance. As a coating material, PU possesses several advantages, e.g. versatility and ease of application, superior chemical and physical resistance, high mechanical strength with flexibility, spray, roller, curtain-coater or electrostatic application, high solid content, transparency, choice of color etc.<sup>16,18,36,40</sup> Nowadays, PU coating is applied on different surfaces and objects, which include building materials, furniture, floor, exterior and interior coating in automobile, coating on metal surface etc. After the development of nanocomposite, it was found that incorporation of nanomaterial not only enhanced the properties of coating polymers, but also introduced several unique attributes which are very useful for many advanced applications. Modern day coating applications require many unique attributes like antibacterial coating, UV-resistant coating, scratch resistance and self-healing coating, self-cleaning coating etc. In this regard, several developments have been reported in the last few years. Li *et al.* (2009) introduced an antibacterial PU/ZnO nanocomposite as coating material for advanced application.<sup>151</sup> Similarly, Sabzi *et al.* (2009) showed improvement of UV protection by preparing PU/TiO<sub>2</sub> nanocomposite.<sup>152</sup> Song *et al.* (2007) prepared PU/MWCNT nanocomposite with excellent wear resistance.<sup>153</sup> Over the last two decades, stress is also given to promote WPU as low VOC containing environment friendly coating material. In recent time, WPU coating are commercially available and used extensively across the globe.

### 1.7.6. Biomedical

PU and PUNC have been widely used in various biomedical applications. PU possesses excellent biocompatibility. PU is extensively used in bone tissue engineering, wound healing, drug delivery, implant material and in the preparation of other artificial biomaterials. One of the early use of PU was as an implant material in pacemaker leads.<sup>154</sup> Polyether based PU was used for this purpose. Nowadays, PU based nanocomposites have been employed in the biomedical domain. Tissue engineering application generally requires 3-D scaffold matrix with target specific bioactivity. PU/HAp nanocomposites are extensively used in this regard. These nanocomposites possess excellent osteogenic activity. Likewise, PU/Fe<sub>3</sub>O<sub>4</sub>, PU/Ag and PU/TiO<sub>2</sub> nanocomposites exhibit profound antibacterial activity and often used as an infection resistance coating material for various medical equipment as well as dressing materials.<sup>35,83,137,138</sup> Many PU based dressings are available commercially, which are used in wound healing and burn injuries. These include PU based dressings like Oponite®, Blisterfilm®, Omnidem®, Epiguard® and Xeroform® etc.<sup>155</sup> Fe<sub>3</sub>O<sub>4</sub> decorated MWCNT/PU has also been reported to be used in antibacterial wound healing application.<sup>35</sup> PU based nanocomposites are further used in targeted drug delivery. A biodegradable LDI based PU showed controlled release of 7-tert-butyl dimethylsilyl-10-hydroxy-camptothecin, an anticancer drug.<sup>156</sup>

### 1.7.7. Optoelectronic

PU is extensively used in electrical and electronic industries as an encapsulator. PU often possesses high mechanical and adhesive strength, excellent water and chemical resistance and desirable dielectric properties.<sup>157</sup> Hence, it is suitable to seal and insulate fragile, pressure sensitive microelectronic components, underwater cables, printed circuit board, transistors etc. On the other hand, PUNCs are used in various advanced optoelectronic applications. Literature demonstrates the use of PU/GO and PU/MWCNT as electromagnetic shielding materials.<sup>158,159</sup> Likewise, GO and CNT can enhance electrical properties, hence PU/GO and PU/CNT nanocomposites are suitable for electrical conducting application. Raja *et al.* (2014) reported electro-active shape memory behavior of a PU/MWCNT nanocomposite.<sup>160</sup> Feng *et al.* (2013) designed PU/graphene nanocomposite as infrared red triggered actuator.<sup>161</sup> In recent

time, PU based nanocomposites have gained interest as light emitting diode (LED). Ummartyotin *et al.* (2012) fabricated bacterial cellulose/PU nanocomposite as organic light emitting device (OLED).<sup>162</sup> Thus, PUNCs are potent candidate in the field of optoelectronics for various modern applications.

### 1.7.8. Smart material

In modern era, PU based materials are of great demand for many advanced applications as smart materials. Smart materials are those designed materials that possess one or more properties which can be significantly altered in a controlled fashion by the application of external stimuli such as stress, temperature, moisture, pH, electro-magnetic wave etc. Generally, it is difficult to obtain pristine PU with such smart attributes. However, incorporation of nanomaterial within a PU matrix can bring about stimuli responsive advanced features like self-healing, self-cleaning, scratch resistance, super hydrophobicity, shape memory etc. Huang *et al.* (2013) reported PU/graphene based nanocomposite as a repeatable self-healing material.<sup>163</sup> Thakur *et al.* (2015) reported a PU/TiO<sub>2</sub> nanocomposite with self-cleaning and self-healing ability.<sup>164</sup> Bayer *et al.* (2010) imparted super hydrophobicity to a PU matrix by fabricating with nano organo-clay.<sup>165</sup> Likewise, Jin *et al.* (2006) described an electro-active shape memory behavior by a PU/CNT nanocomposite.<sup>166</sup> Therefore, PU offers great opportunity to develop smart material through nanotechnology based modification which will create avenue for its unique applications.

## 1.8. Scopes and objectives

State of literature stated in the above sections provides a notion about the recent trend in PU research. It clearly reveals the earnestness to design novel eco-friendly PUNC with unique properties for advanced applications. In this regard, a good number of works has been performed in the form of biodegradable, bio-based and low VOC containing PU. However, this area of PU research needs to be explored further in order to develop PU as a “safe modern age material” by imposing newer environmental and material attributes. Only a small fraction of bio-based raw materials has been utilized in the development of polymeric materials. Most of the literature cited use of vegetable oils as the prime bio-source. However, other plant products like polyphenolic compounds have not been explored sufficiently yet. Thus,

utilization of polyphenol polyols like tannic acid may provide the unique scope for the designing of environmentally benign HBPU. Further, preparation of low VOC containing PU is also desirable to meet the environmental standards. At the same time, it is equally important to improve various properties of these eco-friendly materials by preparing their nanocomposites to meet the modern day demands. In this regard, new and emerging 'green' nanomaterial like CD has not been explored properly. Thus, development of WPU/CD nanocomposite may form the appropriate research proposition to open fresh an avenue for unique applications like photocatalysis, opto-electronic, biomedical etc.

Thus, depending on the ideas procured in the light of literature, following objectives are set for the current investigation:

- (i) To synthesize, characterize and evaluate properties of environmentally benign HBPU.
- (ii) To prepare nanomaterials like GO, CD and HAp by simple conventional routes.
- (iii) To characterize the prepared nanomaterials by using different analytical and spectroscopic techniques.
- (iv) To fabricate and characterize the nanocomposites of HBPU using above nanomaterials at different compositions.
- (v) To evaluate performance of the fabricated nanocomposites for their possible potential applications.
- (vi) To optimize the compositions of the nanocomposites to obtain the best performance for their applications.

### **1.9. Plan of research**

In order to fulfill the objectives of the proposed investigation following plans have been adopted:

- (i) A thorough literature survey in the field of environmentally benign HBPU, CD, GO and HAp and their nanocomposites will be conducted.
- (ii) HBPU will be prepared by using multifunctional moieties like  $\epsilon$ -caprolactam based dihydroxyamine compound and naturally occurring



polyphenol based polyol; diisocyanate like isophorone diisocyanate along with other conventional reactants. Characterization will be done by using different analytical and spectroscopic techniques such as FTIR, NMR, TGA, DSC etc.

- (iii) Nanomaterials like CD, GO and HAp will be prepared through simple conventional techniques.
- (iv) The prepared nanomaterials will be characterized by using different analytical and spectroscopic techniques such as FTIR, XRD, TEM, TGA, etc.
- (v) HBPU nanocomposites will be fabricated by the conventional technique as reported in literature using above nanomaterials.
- (vi) The fabricated nanocomposites will be characterized by FTIR, UV-visible, XRD, SEM, TEM etc. techniques.
- (vii) The performance characteristics of the PUNCs will be investigated.
- (viii) The fabricated nanocomposites will be utilized for their possible potential applications.
- (ix) Optimization of composition of the nanocomposites will be performed to achieve the best performance.

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